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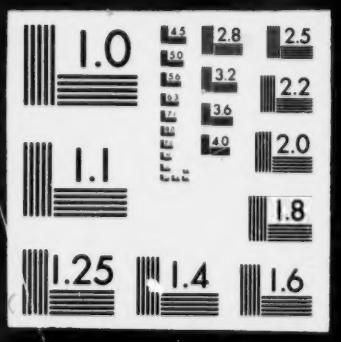

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1971 ANNUAL REVIEW OF LITERATURE. WASTE WATER TREATMENT PHYSICAL AND CHEMICAL METHODS

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1971 Annual Review of Literature

Waste Water Treatment
Physical and Chemical Methods*

Jesse M. Cohen
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Water Reclamation 1972

Increasingly physical-chemical methods are being considered as practical alternatives to conventional biological processes. The literature of 1971 records instances where physical-chemical methods were piloted for consideration at full scale wastewater treatment. The literature on physical-chemical methods published during 1970 was reviewed by Cohen[1]. Barth[2] discussed the relative merits of physical-chemical systems versus biological processes and concluded that, for the near future, the basic technology for municipal wastewater treatment would be biological systems combined with specific physical or chemical processes. A pilot plant study of the system lime clarification, dual media filtration and granular activated carbon was described by Villiers, et al.[3]. The authors showed that lime clarification at pH 9.5 removed 65-70 percent of the organics, 91 percent of the suspended solids and 97 percent of the phosphorus. Carbon removed 60 percent of the applied organics. An economic comparison of the physical-chemical system and activated sludge showed that physical-chemical required less capital but more operating costs than activated sludge but the total overall cost was equal. Graeser[4] reported on the performance of a physical-chemical system treating trickling filter effluent to produce reuseable water. The system consisted of chemical clarification, multi-media filtration

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and granular activated carbon. The average effluent COD of 35 mg/l was considerably higher than that obtained at other tertiary plants. Cherry and Schuessler[5] described the full-scale testing of chemical clarification with ferric chloride and polymer at the Cleveland Westerly plant and demonstrated greatly improved removals of BOD, suspended solids and phosphorus. Pilot studies were conducted on the chemically clarified wastewater using sand and mixed media filters and granular activated carbon. Peacock[6] concluded that physical-chemical processes consisting of chemical flocculation, filtration and granular activated carbon could replace conventional biological processes especially when upsets from toxic chemicals could be anticipated. Activated carbon was shown to remove dissolved organics such as oils, detergents, pesticides and compounds which cause taste and odor.

Kreissl, et al.[7], evaluated the capabilities of a commercially available physical-chemical package treatment plant to treat wastewater on Alaska's North Slope. Raw degritted wastewater was treated by chemical clarification, followed by filtration through two separate beds of granular activated carbon. Median values for product quality were 13 mg/l COD, 5 units of color, 0.8 JTU turbidity and 0.1 mg/l phosphorus. Chlorine, ultraviolet light and iodine were examined for use in effluent disinfection.

Applicability of powdered activated carbon for removal of organics received some attention. In a unique physical-chemical system, Shuckrow, et al.[8], used alum and powdered carbon to treat combined sanitary waste and storm sewer water. Both alum and carbon were recovered for reuse by heat treatment of the sludge and extraction of the ash with sulfuric acid. With an adsorption time of one hour, powdered carbon dosages ranged 500-600 mg/l. Laboratory and pilot plant

studies by Stander, et al.[9], compared performance of powdered versus granular carbon for removal of organics from chemically clarified wastewater. The authors concluded that for applications where the dissolved organic concentrations were relatively low, the powdered carbon system was economically attractive. Similar conclusions were obtained by Peck[10]. Attempts to use a high-rate activated sludge pilot unit to meet New York State quality requirements were unsuccesful but treatment with ferric chloride and 90 mg/l of powdered carbon in a solids-contact clarifier proved to be feasible for the very weak sewage in the city of Hamburg, New York.

Rimer, et al.[11], described the results of pilot plant studies which led to the decision to construct a 15 mgd full-scale facility to treat the combined municipal waste waters from the town of East Fitchburg, Massachusetts, and industrial wastes from two paper mills. The proposed system will include chemical clarification, followed by granular activated carbon. Capital and operating cost estimates were presented.

Phosphorus Removal

Investigations during the past several years on methods to remove phosphates from wastewater have resulted in a number of practical processes. Many of these processes are now ready for application at full scale. Jenkins, et al.[12], have provided an extensive review of the theory and practice of phosphorus removal from wastewater by precipitation techniques. Phosphorus removal merited two major symposia [13,14] at which most known phosphorus removal processes were discussed. Yet another review was published by Pöpel[15]. The removal of phosphorus with ferric or aluminum salts was considered theoretically, and a working hypothesis was formulated and used to derive a mathematical model for estimating the efficiency

of removal. The model was verified for both batch and continuous operation.

Several papers considered the removal of phosphates by metal salt addition to the aerator in the activated sludge process. Zenz and Pivnicka[16] showed that the addition of alum to an activated sludge process in a molar ratio of Al:P of 1.85 resulted in 93 percent removal of soluble phosphorus. Bound phosphorus was not released during anaerobic digestion.

McAchran and Hogue[17] fed alum to an activated sludge plant at a rate programmed to match influent phosphorus and obtained an increase in removal from 71.4 percent to 76.4 percent when a 1:1 Al:P ratio was used. At a ratio of 1:2, 88 percent removal was obtained. According to Thomas[18] the ferric phosphate sludge formed during the precipitation of phosphate by ferric chloride retains the capacity to bind additional phosphate when further ferric chloride is used, thus resulting in a total ferric chloride requirement 1/2 to 2/3 of the otherwise required amount. Ferric phosphate does not dissolve in the digestor. Indeed, further phosphate is insolubilized. Geinopolos and Vilen[19] evaluated several processes for phosphorus removal at Kenosha, Wisconsin. The choice of chemicals, the points of introduction, costs and equipment requirements were discussed in detail.

Further information on the behavior of iron precipitated phosphate in the anaerobic digestor was presented by Malhotra, et al.[20]. They showed that the presence of iron in the sludge, up to about 5 percent iron on a dry solids basis, did not upset or adversely affect the performance of the gas-mixed digestors. Significant release of phosphorus occurred during the anaerobic digestion of waste-activated sludge containing high amounts of ferrous-iron precipitated phosphorus. In contrast, a significant uptake of phosphorus was observed in the digestion of primary sludge containing ferrous-iron precipitated phosphorus.

An investigation was conducted by Recht and Ghassemi[21] of the rate, mechanism and stoichiometry of phosphate precipitation with aluminum and ferric salts from pure phosphate solutions and from secondary effluent. These studies showed that the reactions with orthophosphate are completed in less than 1 second. The pH of optimum orthophosphate precipitation was found to be close to 6.0 for Al(III) and 3.5-4.0 for Fe(III). Similarly, Ferguson and McCarty[22] studied the effect of magnesium and carbonate on precipitation of phosphate by calcium ion, using chemically defined systems. With magnesium present, the phosphate residual decreased, with low values obtained at pH above 9.0. Without magnesium, minimum and maximum residual phosphate were found, respectively, at pH 8 and 9.5.

The kinetics for the removal of orthophosphates from aqueous solutions by activated alumina were examined by Winkler and Thodos[23]. At equilibrium conditions, the derived rate expression reduces to an adsorption isotherm of the Freundlich type. Purushothaman and Yue[24] also investigated activated alumina for the removal of phosphate from wastewater. Using three types of aluminas they determined the capacity to sorb phosphates in the presence of other ions and also studied the effect of flow rate. The exhausted aluminas could be effectively regenerated with 2 M NaOH.

A new approach to phosphate removal was described by Spohr and Talts[25] which consisted of filtration of treatment plant effluent through granular MgO. Results indicated that removal was based on the formation of $Mg_3PO_4 \cdot 5H_2O$ which was firmly bound in the column. Both turbidity and BOD were also reduced. Another novel approach to phosphate removal was described by Recht and Ghassemi[26] who investigated the use of lanthanum salts for ortho- and poly-phosphate removal.

Lanthanum(III) showed a broader effective pH range and lower residual phosphate concentration than Al(III). Within the optimum pH range large settleable flocs were produced. Results suggest a chemical reaction rather than an adsorption process.

Nitrogen Removal

Investigators are recognizing that removal of nitrogen compounds may, in some special areas, be as important as removal of phosphorus. State water quality agencies have lent support to this concept and are establishing nitrogen limits for some streams. Several physical-chemical methods are in various stages of development. Roesler, et al.[27], described a computer program that can be used for the design and simulation of ammonia stripping towers. Detailed capital and operating costs data are included.

A series of papers on nitrogen removal also appeared in a recent symposium[14]. The following physical-chemical methods were discussed in detail: ligand exchange, electrolytic oxidation, cation exchange, adsorption on selective naturally occurring zeolites, air-stripping and oxidation by break-point chlorine treatment.

Adsorption

While activated carbon continues to attract considerable attention as an alternative to conventional biological treatment, the research literature, in contrast, is quite sparse. Usefulness of activated carbon for waste treatment was discussed by Anderson[28]. The theory of carbon adsorption and information on design of contactors are given. The author concludes that carbon treatment of sewage compares favorably with activated sludge. In a somewhat similar approach Lawrence[29] discussed the merits of the use of

activated carbon compared to biological systems. The author suggested that practical application may be restricted because of biological growth in the carbon bed and concluded that more research on the biological aspects of carbon and more information on costs were needed before an acceptable evaluation could be made. Previously reported research by Hopkins, et al.[30], on expanded vs packed beds of carbon is now available as a final report of the study.

Granular carbon has a wide range of applicability and this fact is emphasized by Rizzo[31] who provided case histories of the use of carbon for treating a variety of industrial wastes. Also now available in final report form is the study conducted by Garland and Beebe[32] on the use of powdered activated carbon in recirculating slurry contactor-clarifiers.

Several papers reflect the recognition that methods are needed to characterize carbons and to evaluate their performance. Toward that end Mattson and Kennedy[33] discussed the conventional quality parameters for activated carbons and concluded that these were inadequate. The authors suggested that p-nitrophenol adsorption could be used to assess adsorption capacity and rate of adsorption. Resistance to mechanical attrition could be estimated by shaking carbon on a sieve in the presence of steel balls. Peterson and Lee[34], on the other hand, suggested that capacity and rate of adsorption could best be obtained by using Rhodamine B dye. Hsieh, et al.[35], recognized the importance that bacterial action plays in carbon adsorption and performed batch adsorption tests in an attempt to quantitate the rate of decay of adsorbed organics. Their results established that the system could be characterized by a Freundlich type adsorption isotherm and that the decomposition of organic solutes by bacteria conformed to a modified first

order rate expression. Thermal regeneration of powdered carbon, use of expanded-bed adsorption and pilot scale testing of granular activated carbon were subjects covered in a symposium on advanced waste treatment methods[13].

Coagulation-Flocculation-Sedimentation

The utility of coagulation followed by flocculation and sedimentation for removal of a variety of pollutants from wastewater is evidenced by a number of studies published in the last year. Bagot[36] reported on the use of ferric chloride, sea water and polymers to substantially upgrade primary treatment of San Francisco sewage. Neither alum nor lime was particularly effective for this sewage. Nilsson[37] obtained excellent removal of a variety of heavy metals with lime treatment of sewage to pH 9.5 as well as alum coagulation of the sewage. Lime was more effective than alum in terms of degree of removal and variety of metals removed. Linstedt, et al.[38], reported similar results and extended the studies to include many other advanced waste treatment processes.

Solids removal, employing coagulation and flocculation techniques, as a procedure for upgrading conventional treatment continues to be of interest. Stukenberg[39] found that lime coagulation of high rate activated sludge effluent (HRAS) could yield an effluent superior to that of conventional activated sludge. The cost of this technique (18¢/1000 gal)(4.8¢/cu m) is considerably less than conventional secondary plus tertiary treatment. Upgrading oxidation pond effluent with alum, and ferric compounds was studied by Shindala and Stewart[40]. In addition to 90 percent removal of phosphorus and 70 percent removal of COD, significant removal of algal cells was obtained. They derived an empirical relationship between phosphorus concentration and required alum dose.

Studies of removals of somewhat esoteric pollutants in pure water systems

were reported by two groups of investigators. Virus removal with ferric chloride and/or alum could reach 99.5 percent[41]. However, the virus particles were not inactivated by this treatment; thus care must be exercised in sludge disposal. In addition, it was found that organic material in the water could interfere with virus removal by coagulation. Cassell, et al.[42], studied microflotation in the presence of aluminum salts as a procedure for removal of colloids. Best results were achieved at pH ranges in which the aluminum salts were insoluble.

Control and improvement of these solids removal processes by physical techniques is now receiving increased attention. The importance of rapid mix in conjunction with chemical treatment was studied by Vrale and Jorden[43]. It was found that a tubular reactor is better than a back-mix type and that the root-mean square velocity gradient is inadequate for characterization of rapid mix efficiency. Coagulation control by electrical conductivity was tested for algae coagulation by alum and lime precipitation of phosphorus. Some indication of the advantages of this procedure were pointed out by Pavoni and Eichelberger[44]. A study of the behavior of flocculent suspensions in sludge blanket clarifiers indicated that the same functional relationship as previously determined for discrete particles could be applied[45]. Improvement in performance of sedimentation basins receiving raw wastewater and biological treatment liquor by the installation of tube settlers was studied by Slechta and Conley[46]. Overflow rates in the range of 3 gpm/ft^2 (122 l/min/sq m) to 6 gpm/ft^2 (244 l/min/sq m) were found feasible.

Excellent State-of-the-Art reviews of coagulation and flocculation were published by Jorden[47] and AWWA Research Committee[48]. The latter concentrates on the chemistry of coagulation and includes 88 significant references.

Filtration

The last decade has seen a significant increase in the application of filtration to wastewater treatment. Coincident with this trend have been studies into the basic mechanisms of the process. The latest of these is the work of Yao, et al.[49], in which particle destabilization and particle transport are featured as the primary mechanisms. The model of these investigators indicates that diffusion is important for removal of small particles while larger particles are removed by interception and sedimentation. An alternate modeling procedure to the school which develops filtration equations from first principles is the use of empirical models. Huang and Baumann[50] used such a model to optimize sand filtration design for removal of iron from water.

The most widespread application of filtration in wastewater treatment is for upgrading the effluent from activated sludge or trickling filter plants. Tebbutt[51] found that flow rate had little effect on filter performance but sand size was significant. A medium size sand (1.2-2.4 mm) gave the best combination of good solids removal and a low rate of pressure increase. Michaelson[52] achieved 65 percent to 75 percent suspended solids removal with an upflow filter at flows of 5 gpm/ft^2 to 8 gpm/ft^2 (204 to 326 l/min/sq m). Better results were obtained when the trickling filter plant preceding the filter was underloaded. Backwash water volume required was only 1.5 percent of the total flow. Guiver and Huntingdon[53] evaluated two upflow filter designs in parallel with a radial flow filter for filtration of the effluent from a poorly nitrifying activated sludge. All three filters provided 80 percent removal of suspended solids at 5 gpm/ft^2 (204 l/min/sq m). The reference above to a radial flow filter is indicative of new concepts in filter design. Bell, et al.[54], reported on

another new concept, the moving bed filter (MBF). This filter was used to treat unsettled trickling filter effluent, primary effluent and raw sewage. Alum was used as a coagulant but was applied directly to the filter inflow. One basic concept of the MBF is to eliminate in situ backwash of the filter media. The importance of backwash in static bed filters was reviewed by Camp, et al.[55]. This article presents an excellent review of the theory of fluidization of granular media in water and air-water systems.

A modification of reverse osmosis has been adopted as a new filtration technique called ultrafiltration. Membranes considerably more open than those used for salt rejection are employed for colloid and large molecule removal. This process can also be employed for solids separation and recovery in highly concentrated suspensions. Hardt, et al.[56], employed this process for solids separation rather than a secondary tank with activated sludge. The positive nature of the solids separation here allows development of MLSS values of 20,000 to 30,000 mg/l. Desaulniers and Hausslein[57] utilized ultrafiltration to dewater spent powdered, activated carbon.

Demineralization

Ion exchange and reverse osmosis have emerged as the leading processes for demineralization of wastewater. Recent studies have concentrated on ancillary factors such as degree of fouling and removal of other pollutants rather than specifically on demineralization performance. Dhond[58] studied BOD, suspended solids, nitrogen, TOC, and BOD removal with strong base anion exchange resins. Grantham and Robertson[59] studied fouling of both anion and cation resins by microstrained secondary effluent. Fouling by detergents both reduced the exchange capacity and increased the rinse water requirements. Chemical cleaning restored the resin capacity.

Although ion exchange is in general cheaper than reverse osmosis for demineralization, reverse osmosis has greater potential for overall waste treatment. Golomb and Besik[60] reviewed the various reverse osmosis configurations and the process applicability for industrial wastes. Feuerstein and Bursztynsky[61] evaluated reverse osmosis for treatment of municipal wastewater at all stages of conventional treatment. In addition the sewage was subject to chemical treatment prior to reverse osmosis. In all cases excellent removal of all pollutants was obtained with a varying degree of membrane fouling. Based on the results a model of flux decline as a function of organic concentration and suspended solids was formulated. A general review of the design details of reverse osmosis equipment was made by Bezik[62]. He concentrated on the membrane support structure. The disposal of the concentrate stream from the reverse osmosis process is often overlooked. Jennett and Patterson[63] found that activated sludge and chemical treatment could be used for this purpose.

Fouling of reverse osmosis membranes is a critical factor in design and operation. Harsh cleaning agents cannot be used to reverse fouling due to the delicate nature of the cellulose acetate membrane surface. Consequently alternate membrane materials are being sought. Porous glass membranes were investigated and were found to have some promise[64]. Kraus[65] investigated a unique system in which membranes were dynamically formed from polyelectrolytes and the constituents of sewage. While this system does not preclude fouling, it makes membrane replacement extremely economical.

It appears that reverse osmosis will require significant development before it can be economically applied to waste water treatment on a large scale.

Miscellaneous

Recent research activity in the use of ozone for waste treatment indicates that this process will soon play an expanded role in treatment technology. A limited review of this field was presented by Lowndes[66]. McNabney and Wynne[67] discussed the advantages of ozone for treatment of secondary effluent and presented cost estimates for plants from 1 MGD to 100 MGD (3785 to 378,500 cu m/day). In the range of 35 mg/l to 15 mg/l COD, the ozone requirement was 1.25 mg/l per 1 mg/l of COD destroyed. Hewes and Davison[68] reviewed the chemistry of ozone decomposition. pH had the major effect with the kinetics quite rapid at pH values above 6. Steinberg and Beller[69] evaluated the use of atomic radiation to produce ozone. They concluded that when large quantities are required (hundreds of tons per day) nuclear radiation of O_2 was by far the most economical source.

Catalytic oxidation of organics in waste water was facilitated by ultrasonics according to Smith, et al.[70]. Fisher[71] obtained some success using air heated to 300° to 400°C to oxidize carbon compounds in sewage. Acetate as well as ammonia were, however, refractory.

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